UNIVERSITY OF PITTSBURGH SECOND SEMI-ANNUAL REPORT FOR NASA GRANT NSG-416 COVERING THE PERIOD I MAY 1964 THROUGH 31 OCTOBER 1964

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SUBMITTED BY

SPACE RESEARCH COORDINATION CENTER

1 NOVEMBER 1964

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University of Pittsburgh

Second Semi-Annual Report

for

NASA Grant NsG-416

covering the period

1 May 1964 through 31 October 1964

Submitted by

Space Research Coordination Center

1 November 1964

David Halliday Acting Director This report contains (1) a summary of research performed in which substantial support came from grant NsG-416; (2) a listing of NASA Postdoctoral Fellows; (3) a listing of NASA Predoctoral Trainees; (4) a report of new faculty added in space-related research areas; and (5) biographies of new NASA-SRCC appointees.

APPLICATIONS OF THERMODYNAMICS TO METALLURGICAL PROCESSES

The University of Pittsburgh has recently established a Center for the Study of Thermodynamic Properties of Materials. This Center is under the direction of Dr. G. Raymond Fitterer, (formerly Chairman of the Metallurgical Engineering Department and Dean of the Schools of Engineering and Mines).

In line with this development, Dr. Oswald Kubaschewski, Senior Principal Scientific Officer of the National Physical Laboratory in Teddington, Middlesex, England, has come to the University as a Visiting Professor to teach and serve as a consultant to the Center.

In addition, Dr. Leslie L. Seigle, Head of the Metal Physics Group of the General Telephone and Electronics Laboratories, Bayside, New York, will also serve as a Visiting Professor during the current school year.

Mr. Robert J. King of the Applied Research Laboratories of the U.S. Steel Corporation and Mr. Charles J. Kubit of the Atomic Power Division of Westinghouse have been given leaves of absence from their companies for extended periods so as to assist in this development. A number of graduate students from here and abroad are also actively engaged in the program.

This Center is dedicated to the determination of fundamental properties of materials and to their practical applications through the use of thermodynamic principles. It is sponsoring a conference on this subject on November 30 and December 1, 1964. The program is:

Monday, November 30, 1964

8:00 to 9:30 a.m.	REGISTRATION, Mellon Institute Auditorium
9:30 a.m.	OPENING REMARKS by Dr. G. R. Fitterer, Conference Chairman
9:45 a.m.	"Welcome to the Conference," Dr. E. H. Litchfield, Chancellor, University of Pittsburgh

10:00 a.m.

PANEL I: "The Current Status and Availability of Fundamental Thermodynamic Data"

<u>Chairman:</u> <u>Dr. Frederick D. Rossini,</u> <u>Dean, College of Science, Notre Dame</u> University

- 1. Dr. Ralph Hultgren, Professor of Metallurgy, University of California (Berkeley). "Additional Data Needed to Establish the Thermodynamic Properties of Alloying Systems."
- 2. <u>Dr. Oswald Kubaschewski</u>, Senior Principal Scientific Officer, National Physical Laboratory, Teddington, Middlesex, England. "The Calculation of Phase Boundaries in Metallic Systems."
- 3. Dr. John Chipman, Professor of Metallurgy (Emeritus),
 Massachusetts Institute of Technology. "Activities and Activity Coefficients in Metallic Solutions and Relations to Metallurgical Processes."
- 4. Dr. C. B. Alcock, Reader in Chemical Metallurgy, Imperial College of Science and Technology, University of London; currently Visiting Professor, North Carolina State University. "Dilute Solutions in Metals and Alloys with Particular Reference to Oxygen and Sulfur."
- 5. Dr. Everett R. Johnson, Office of Standard Reference Data, National Bureau of Standards.

 "The National Standard Reference Data Program Historical Development and Current Status."
- 6. <u>Discussion</u>
- 7. Summary and Closure <u>Dr. F. D.</u>
 <u>Rossini</u>

12:30 to 2:00 p.m.

LUNCHEON A special luncheon for all conferees has been arranged at Webster Hall. In addition, the cafeteria in Schenley Hall is available.

2:00 p.m.

PANEL II: "Applications of Thermodynamic Principles to Metallurgical Systems"

Chairman: Dr. W. E. Wallace, Chairman Department of Chemistry, University of Pittsburgh

- 1. Dr. G. W. Mellors, Research
 Scientist and Dr. S. Senderoff,
 Senior Scientist, Parma Research
 Laboratories, Union Carbide
 Company. "Electrode Reactions in
 the Electrolysis of Fused Salts."
- 2. <u>Dr. B. Meddings</u>, Assistant Head, Research Division and <u>Dr. V. N. Mackiw</u>, Director, Research and <u>Development Division</u>, Sherritt-Gordon Mines, Alberta, Canada. "The Gaseous Reduction of Metals from Aqueous Solutions."
- 3. Dr. Irving Johnson, Associate Chemist, Chemical Engineering Division, Argonne National Laboratory. "Partition of Metals between Liquid Metal Solids and Fused Salts."
- 4. Dr. T. R. Ingraham, Head, Research Section, Canadian Mines Branch, Ottawa, Canada. "Sulphate Stability and Phase Diagrams with Particular Reference to Roasting."
- 5. Dr. J. J. Ward, Research Associate,
 Dr. J. H. Oxley, Assistant Division
 Chief, Battelle Memorial Institute,
 Columbus, Ohio, and Mr. A. D.
 Coon, Graduate Assistant, The
 Ohio State University, Columbus,
 Ohio. "Preparation of Pure
 Tungsten Metal from the Reactions
 of Tungsten Hexa-carbonyl with
 Mixtures of Hydrogen and Steam."

- 6. Discussion
- 7. Summary and Closure \underline{Dr} . \underline{W} . \underline{E} . Wallace

6:00 p.m.

RECEPTION AND DINNER, Georgian Room, Hotel Webster Hall

CONFERENCE ADDRESS: Dr. O. Kubaschewski, "The Next Ten Years in Chemical Metallurgy"

Tuesday, December 1, 1964

9:30 a.m.

PANEL III: "Applications of Thermodynamics to Metallurgical Systems" (continued)

Chairman: Dr. J. Alfred Berger, Chairman, Metallurgical Engineering Department, University of Pittsburgh

- 1. Dr. George R. St. Pierre,
 Professor, Metallurgical
 Engineering, The Ohio State
 University. "Free Energy Balance
 in Process Analysis."
- 2. Dr. C. W. McCoy, Senior Research
 Scientist; Mr. A. F. Kolek,
 Metallurgical Technician; and
 Dr. F. C. Langenberg, Director,
 Process Research and Development
 Laboratory, Crucible Steel Company
 of America. "Application of
 Thermochemical Data During Stainless Steel Melting."
- 3. Dr. Paul Gilles, Professor, Chemistry
 Department, University of Kansas.
 "Thermodynamic Analysis of Materials
 at High Temperatures and Low
 Pressures."
- 4. Dr. G. R. Fitterer, Distinguished
 Professor, Metallurgical
 Engineering and Director of the
 Thermodynamics Center, University
 of Pittsburgh. "A Summary of
 Experiences in Applying Thermodynamics to Metallurgical Processes."

- 5. Discussion
- 6. Summary and Closure <u>Dr. J. A.</u>
 <u>Berger</u>

12:30 to 2:00 p.m.

Lunch, Hotel Webster Hall

2:00 p.m.

PANEL IV: "Needs for Future Applications of Thermodynamics"

Chairman: Dr. J. F. Elliott,
Professor of MetalTurgy, Massachusetts
Institute of Technology, Cambridge,
Massachusetts

- 1. Dr. Charles E. May, Head,
 High Temperature Chemistry
 Section, Lewis Research Center,
 National Aeronautics and Space
 Administration, Cleveland, Ohio.
 "Requirements in Space Materials."
- 2. <u>Dr. P. T. Stroup</u>, Assistant <u>Director of Research</u>, Aluminum Company of America, New Kensington, Pa. "The Aluminum Industry."
- 3. <u>Dr. H. H. Kellogg</u>, Professor of <u>MetaIlurgy</u>, Columbia University, New York City. "Problems in the Non-ferrous Industries."
- 4. Professor William O. Philbrook,
 Metallurgical Engineering
 Department, Carnegie Institute of
 Technology, Pittsburgh, Pa. "Needs
 in the Basic Oxygen Furnace Steel
 Process."
- 5. <u>Dr. J. E. Fogarty</u>, Assistant to the <u>Superintendent</u>, Smith Division, Republic Steel Co., Canton, Ohio. "Vacuum Degassing of Liquid Steel."
- Manager, Homer Research Laboratories, Bethlehem Steel Company, Bethlehem, Pa. "The Problems in Continuous Casting."

- 7. Discussion
- 8. Panel Summary by Dr. Elliott
- 9. Closure by the Conference Chairman

THEORETICAL STUDY OF FLOW SEPARATION by

R. K. Duggins, NASA Postdoctoral Fellow in Mechanical Engineering

An investigation in the field of aeronautics has been initiated, the aim being to gain further knowledge on the theoretical treatment of flow separation. It is flow separation which limits the performance of many fluid mechanisms so that a better understanding of the phenomenon would clearly have very far-reaching application.

Previous work on this topic has been based on two distinct potential flow theories—the free streamline theory and the trapped vortex theory. In the former, it is assumed that the dividing streamline, which bounds a separation region, may be regarded as one of the flow boundaries and as a contour of constant velocity and pressure. On the other hand, the trapped vortex theory makes no such assumption and, instead, account is taken of the separation region as an integral part of the overall flow pattern. This is done by regarding the mechanism of separation and reattachment as a potential flow phenomenon and by representing the circulation of fluid within the separation region as a trapped vortex.

Neither theory gives entirely satisfactory results, although each one has attractive features. For example, a classical free streamline analysis enables the profile of a dividing streamline to be accurately located, whereas a trapped vortex analysis gives a better representation of the reattachment process which often forms a sequel to flow separation.

The possibility of fusing the two methods into a single composite one is being investigated in the hope that the attractive features of both of the basic theories might be retained. An intensive search of the literature suggests that this line of attack has not been investigated, but the prospects seem very promising.

POLYSACCHARIDE SYNTHESIS IN CRYPTOCOCCUS LAURENTII by
Helmut Ankel, NASA Postdoctoral Fellow in Biology

Background Information and Statement of Problem

Biological macromolecules can be considered as members of two main classes--nucleic acids and proteins on the one hand and polysaccharides on the other. Proteins and nucleic acids are linear polymers which are synthesized in accordance with a template mechanism whereas polysaccharides are (often) branched polymers whose formation does not involve a template. As far as is known, the synthesis and structure of polysaccharides are regulated by the supply of terminal precursors (building-block donors) as well as by the specificity of the enzymes which mediate transfer of the glycosyl moieties (building blocks) from terminal precursor to the growing polymer chain.

We have chosen to investigate as a model system the synthesis of the extracellular polysaccharides of Cryptococcus laurentii, a non-fermentative yeast. The capsule contains the hexose D-mannose, the hexuronic acid D-glucuronic acid, and the pentose D-xylose. The xylosyl and glucuronosyl residues are always located at the end of branched chains of mannose units in this polymer. Xylose, therefore, seems to be one of the key compounds in the synthesis of this polymer, since, as soon as a chain accepts a xylosyl or glucuronosyl moiety, it cannot grow any more.

When this project was initiated, it was assumed that the donor of the xylosyl residue was uridine diphosphate D-xylose (UDPxyl), of the glucuronosyl residue UDP glucuronate (UDPGA), and of the mannosyl residue guanosine diphosphate mannose (GDPM). In addition, based on previous findings with higher plants, it was assumed that UDPGA was enzymatically decarboxylated by the organism to form UDPxyl. Such a situation would be expected to establish adequate control of the synthesis and structure of the polymer since the concentration of UDPxyl and the UDPxyl/UDPGA ratio would control the direction and extent of synthesis.

Projected Program

In order to be able to investigate details of regulation and synthesis of the polymer it was first necessary to establish the basic soundness of our hypothesis. This would have to involve isolation of the hypothetical terminal precursors of polymer synthesis

from the Cryptococcus cells and demonstration of the postulated reactions leading to the formation and utilization of the terminal precursors of polymer formation. At present, a number of individuals are working on various aspects of the problem: on reactions leading to conversion of simple sugars to nucleoside diphosphate sugars, on reactions leading to formation of terminal precursors, and on reactions leading to glycosyl transfer into polymer from these precursors.

Progress to Date

During the tenure of my NASA fellowship, I have been investigating the formation of terminal precursors. Pertinent specific details are given in the progress reports of 1 December 1963, and 1 May 1964. progress reports are abstracts of presentations at scientific meetings. In summary, I succeeded in demonstrating the presence in Cryptococcus laurentii of most of the postulated terminal precursors of polymer synthesis. (These findings have been published in Biochim. Biophys. Acta 90, 397 (1964).) In addition, I succeeded in purifying the enzyme responsible for formation of UDPxyl from UDPGA. In this stage of the work the surprising observation was made that the reaction required catalytic quantities of the coenzyme NAD and that it was inhibited by NADH2. The implications of these findings are fundamental and far-reaching. Since NADHo inhibits the formation of UDPxyl, the concentration of NADHo controls the UDPxyl/UDPGA ratio and thereby controls the synthesis of the polymer.

Discovery of the need for NAD lends support to the view that 4-keto-UDPGA is an intermediate in the decarboxylation. Such a compound, with a keto group at the 4 position of the glucuronosyl residue, β to the carboxyl group, i.e.,

is a β keto-acid. In such compounds decarboxylation is favored. The role of the NAD in the reaction may be to cause the transient formation of the 4-keto compound by acting as a reversible H acceptor.

Since UDPGA decarboxylation was first studied in higher plants, it was of interest to compare the enzyme

from plants with the cryptococcal enzyme. To this end, I have purified the comparable enzyme from Wheat Germ. The purified protein, which has been obtained in a crystalline fraction, showed no NAD activation, nor was it inhibited by NADH2. Possibly the plant enzyme does contain NAD, but it is very firmly bound.

Plans for the Future

I expect to continue my studies of the mode of action of the purified enzymes from the two separate sources, yeast and plant, and hope to be able to throw some light on the mechanism of the reaction.

Significance of this Research

The results reported here have general significance in many areas of biology and biochemistry.

Data of importance to comparative biochemistry and evolution of macromolecules will result from consideration of UDPGA carboxy-lyase from two sources, yeast and higher plants.

It will be possible to correlate my findings with studies on similar NAD-activated enzymes such as UDP-glucose-4-epimerase, in which the role of NAD is not completely clear.

Information will be obtained, having bearing on control mechanisms especially the role of the NAD/NADH2 ratio in regulation of synthetic reactions.

INFECTIVITY OF DNA ISOLATED FROM BACTERIOPHAGE SP82 by

D. MacDonald Green, Associate Professor of Biology

Since the initial proposal was offered, research has been undertaken at the University of Pittsburgh on several aspects of the proposal, and the initial report on the Infectivity of Bacteriophage SP82 DNA has been written and accepted for publication in the Journal of Molecular Biology.

The present research that has been accomplished here concerns specific attempts to correlate the genetic map distances of the bacteriophage genome with the physical size of the molecule of DNA that bears the genetic information. Although the physical studies of the bacteriophage DNA molecular sizes were accomplished at Harvard University all of the biological data reported herein has been done at the University of Pittsburgh.

The question at hand is to determine whether there is any correlation of the map distances with the physical size of the DNA molecule. To ask this question it is first necessary to have DNA molecules of different sizes. Burgi and Hershey (1) have developed techniques for specifically breaking bacteriophage DNA molecules into half pieces. We have been able to confirm their observations with the DNA of our bacteriophage. When bacteriophage SP82 DNA is stirred at the proper speed in a microhomogenizer the molecular weight undergoes a discreet shift from a molecular weight of 120 x 10^6 daltons to half this value, 62×10^6 daltons.

Using the sheared and unsheared DNA's in biological assays we can determine the effect of the shearing on the ability of the DNA to contribute genetic markers. This is possible by using wild-type bacteriophage DNA (sheared or unsheared) to infect bacterial cells and subsequently "rescuing" this DNA by superinfection of the bacterium with a mutant bacteriophage. If we plate, the now superinfected, cells under conditions where the superinfecting phage will not plate, those plaques arising will be the result of recombination between the superinfecting phage and the infective DNA. In this manner the sensitivity of shear of various single mutant markers and pairs of mutant markers can be determined. Since the linkage distances between the pairs of markers has been determined by genetic mapping, and all markers are linked in this system, it is then possible to plot the sensitivity of the marker or marker pairs against the fraction of the genetic map that the marker or marker pair subtends. Analysis of the data thus generated shows a direct correlation between the map

distance between markers and the sensitivity to shearing into half pieces. Since the initial and half molecular weights of the DNA have been determined it is possible to present this plot as the fractional survival for any marker or marker pair as a function of molecular weight. Such a plot of the molecular weight at which an e⁻¹ survival is achieved as a function of the map distance between markers is presented.

This plot has the following characteristics: 1) It extrapolates to the known molecular weight of the phage where marker pairs are at opposite poles of the genome. This is expected since the shearing events tend to occur at the center of the molecule and will thus unlink all marker pairs separated by exactly half of the total map distance. 2) There is a direct proportionality between the fraction of the total genome that a marker pair subtends and the molecular weight that an e-1 survival is achieved. Thus, the genetic distance is proportional to molecular distance for the marker pairs examined. This is again expected since the probability of a marker pair spanning the position of the shear event will be directly proportional to the length of the molecule between the two genes. 3) The molecular weight extrapolated at zero genome fraction subtended is of the order of 40×10^6 daltons. The exact reasons for this observation are not clear. However, it is reasonable to assume that the frequency with which non-central breaks occur, and the area of damage caused by a scission and, as well, the minimum molecular weight of DNA that can cooperate in an exchange event will also effect this parameter.

These observations yield the following conclusions about the genetic structure of the SP82 bacteriophage:

1) the genetic map is circularly permuted in respect to the physical molecule, and 2) recombination events occur (over the relatively long molecular distances measured here) proportionally to the molecular distance between markers.

(1) E. Burgi and A. D. Hershey, J. Mol. Biol. 3, 458 (1961).

GENETIC AND BIOCHEMICAL EFFECTS OF RADIATION ON SOMATIC CELLS

by

S. Venketeswaran, NASA Postdoctoral Fellow in Biology

The objectives of the present investigations were to study the influence of environmental and cultural conditions on the photosynthetic mechanism. For these studies, somatic cells of albino mutants of tobacco grown in sterile culture were employed.

"Albinism" in tobacco, which is controlled by duplicate genetic factors for chlorophyll production, represents a lethal character under normal conditions of plant development and is phenotypically expressed by the absence of chlorophyll. With tissue culture techniques and supplemental carbohydrate nutrition, in the present work it has been possible to overcome this lethality at the cellular and callus levels of organization.

Proliferating albino callus tissue cultures in a totally-defined salt-sucrose medium are continuously maintained for further experimentation. Patches of green chlorophyllous areas, which appear on albino callus growing under low intensities of illumination when isolated and grown, continue to remain green indicating the capacity of the albino cells for chlorophyll production under specific culture conditions.

Irradiation experiments on albino plant material from a Cs137 source showed that the callus cultures are more radioresistant than the 10-12 day-old germinated seedlings or axillary buds from mature seedlings in culture. After an irradiation of 7800 r, liquid suspensions when plated on agar failed to produce any colony growth whereas morphological effects on seedlings were evident after an irradiation of only 500 r. More experiments are in progress for evaluating and isolating mutant colonies which may have one or more blocks in their chlorophyll pathway and biosynthesis.

"Green-pigmented callus" isolated from known genetic strains of tobacco possessing the specific genotype for chlorophyll production develop normal chloroplast differentiation depending on the chemical and physical nature of the culture conditions. The growth factors incorporated in the culture medium influenced considerably the qualitative and quantitative expression of chlorophyll, viz., deletion of 2,4-dichlorophenoxyacetic acid (2,4-D) and addition of kinetin increased chlorophyll production. Chlorophyll destruction and bleaching were very evident under strong intensities of light whereas low intensities

S. Venketeswaran Page 2

of light provided by Sylvania 'Gro-Lux' illumination favored the development and functioning of a normal photosynthetic apparatus.

Electron microscopic observations of chloroplasts in cells of normal green callus revealed a typical grana and stroma lamellar system as in chloroplasts of normal leaves. Detailed analyses of the cells from albino plants and from albino callus are at present in progress. It will be thus possible to demonstrate the physiological expression of chlorophyll synthesis and chloroplast differentiation from biochemical studies and from details of ultrastructure.

In summary, it has been possible to demonstrate (i) that "albinism" which represents a 100 per cent lethal character can be overcome by using specific culture techniques and by supplemental carbohydrate nutrition; (ii) that such albino cells in culture can show normal chlorophyll synthesis and chloroplast differentiation under specific culture conditions; (iii) that cultured cells are more radioresistant than seedlings or buds from mature plants and thus afford a better way to approach biochemical studies on photosynthetic mechanism; (iv) that chlorophyll synthesis and chloroplast differentiation in normal green cells in culture will depend on the chemical and physical nature of the culture and (v) that it is possible to relate physiological expression of chlorophyll synthesis with ultrastructure analysis of chloroplast differentiation in cultured cells.

This work complements similar studies being carried out in other systems in this laboratory. An ultimate objective in the total program is the study of genetic factors at the somatic cell level. The utilization of known genetic mutants provides a relatively well defined point of departure in this study.

STRUCTURE OF DINAPHTHOQUINONE by

Elli Hand, NASA Postdoctoral Fellow in Chemistry

The structure determination of the alleged "monohydrazone" of dinaphthoquinone was continued. It was found that the compound, tentatively assigned structure I, could also be prepared by treatment of naphthoquinone itself with hydrazine. Its elemental analysis, $C_{20}H_{10}O_3N_2$, shows clearly that Pummerer's hydrazone structure is incorrect. Of the oxidation products only one, phthalic acid, has so far been identified. Reduction, even under acylating conditions, has yielded only unstable products. As regards the alternate unambiguous synthesis, the "coupling product" II has now been obtained. Under various reduction conditions the N-N bond of II is cleaved, as shown by the formation of aniline; spectral evidence indicates that compound III, which has not been obtained in a pure state or in good yield, can be formed. It is expected that diazotization of III followed by reduction will yield compound I. After the structure of the "monohydrazone" has been established, its possible charge-transfer properties will be investigated.

As a consequence of a chance observation, a series of nuclear magnetic resonance studies was carried out on interactions of organic compounds in aqueous solutions. The effect of the diamagnetic anisotropy of aromatic compounds permitted the monitoring of the interactions. Aggregates are formed by hydrophobic bonding. The extent of aggregate formation parallels approximately the concentration of the aromatic material and the nonpolar character of the organic compounds. Thus, the chemical shift of compounds generally used as standards in aqueous solution is strongly affected by the presence of the aromatics (phenanthrene and naphthalene derivatives). N.M.R. may become a useful tool for studying hydrophobic bonding in properly selected systems.

STATISTICAL INFERENCE FROM RADIOACTIVITY MEASUREMENTS by
Edgar Inselberg, NASA Postdoctoral Fellow in Chemistry

Flash Spectroscopy of Porphyridium

The spectrum of flash-induced absorption changes in Porphyridium was investigated. The main feature was a relatively large negative change at 420 mm, attributed to the photo-oxidation of the cytochrome f pigment system. The demonstration of a positive absorption change at 520 mm points to the similarity in the primary photosynthetic steps between this alga, a representative of red algae, and the more intensively studied green algae, such as Chlorella.

The absence of a negative change at 475 mµ, accompanying the 520 mµ change in Chlorella, was explained in this paper. The anticipated change at 475 mµ is apparently compensated by a positive change accompanying the photo-oxidation of cytochrome f, which is the system associated with the most prominent flash-induced changes in Porphyridium.

The use of statistical criteria (fiducial probability) in the field of flash spectroscopy, in place of purely subjective criteria, to indicate the significance that can be attached to very small changes in absorbance (10-3 to 10-4 absorbance units), is a methodological innovation introduced in this paper.

Data on the half-life, type of decay, magnitude and band width of the 520 mµ change in Porphyridium strongly indicate that this change is attributable to the same, or similar, pigment system as the 515 mµ change in green algae. These findings have, therefore, clarified what was hitherto considered, on meager evidence, to be a puzzling departure of red algae from photosynthetic schemes worked out from research on green algae. (1)

Current Project: Statistical Inference from Radioactivity Measurements.

- A. Work prior to present report:
 - 1. Literature review.
 - 2. I familiarized myself with recent developments in instrumentation, including space applications.
- B. Work since the last report:
 - 1. The literature review was brought up to date.
 - 2. Recent textbooks in applied statistics were studied to review the mechanics, underlying assumptions and applicability of various statistical tests.

- 3. Pertinent topics in mathematics were reviewed, in preparation for the derivation of a mathematical model for the variability of radioactivity measurements.
- C. Objectives and future plans:
 - 1. To derive a mathematical model for the variability of radioactivity measurements that will furnish:
 - a. The frequency distribution function(s).
 - b. The mean, standard deviation and higher cumulants.
 - c. A method for partitioning procedural variability (that not attributable to the randomness of disintegration which is distributed in a Poisson series) into its components.
 - 2. To apply this model in determining appropriate procedures for:
 - a. Obtaining confidence intervals.
 - b. Statistical test: tests of significance, goodness of fit, analysis of variance.
 - c. Selection of counting systems, considering procedural errors.
 - d. Optimum distribution of counting time between sample and background, taking into account procedural errors.
 - 3. Experimental: Testing the validity of the mathematical model using statistical criteria of goodness of fit.
- (1) E. Inselberg and J. L. Rosenberg, Plant Physiol. 39, 810 (1964).

RESEARCH IN CRYSTALLOGRAPHY

bу

Truman H. Jordan, NASA Postdoctoral Fellow in Chemistry

Since I began my research on September 1, no really tangible results are evident as yet. However, work is progressing on two projects.

One project is the solution of the crystal structure of H₂CO₃·Et₂O. Since the compound decomposes at -10°C, the problem presents certain experimental difficulties. The compound has been prepared by known methods; however, no crystals suitable for x-ray analysis have been obtained yet.

The other project is building a completely automated counter suitable for single crystal x-ray work. Much of the equipment needed is already available here in the Crystallography Laboratory and it is merely in need of minor repairs. Other equipment needed will have to be purchased and work is proceeding in this direction.

POLYHEDRAL CLATHRATE HYDRATES by Thomas C. W. Mak, NASA Postdoctoral Fellow in Crystallography

The structure of the tetrahydrofuran/hydrogen sulphide double hydrate has been determined from three-dimensional single crystal data. The analysis confirmed the clathrate host lattice characteristic of 17A cubic (Structure II) gas hydrates (1). Statistically 46 per cent of the pentagonal dodecahedra are occupied by hydrogen sulphide molecules, whereas the larger hexakaidodecahedral voids enclose tetrahydrofuran molecules which appear to undergo free rotation.

Recently Dr. G. A. Jeffrey, Dr. R. K. McMullan and I have started an investigation on the hydrates of simple aliphatic amines, a remarkable series of crystalline compounds first characterized by Pickering (2) in 1893. A preliminary survey of the crystal data is in progress, and it is hoped that detailed x-ray analyses of representative members of this class of compounds will reveal still further structural types in addition to those already known for the gas hydrates and the peralkylated ammonium salt hydrates.

- (1) W. F. Claussen, J. Chem. Phys. <u>19</u>, 259 (1951); M. v. Stackelberg and R. H. Müller, Z. Electrochem. <u>58</u>, 25 (1954).
- (2) S. U. Pickering, Trans. Chem. Soc. 63 I, 141 (1893).

THE BEHAVIOR OF HIGH-ENERGY INTERMEDIATES IN ORGANIC SYSTEMS

bу

Jack Pinkus, NASA Postdoctoral Fellow in Chemistry, and Theodore Cohen, Associate Professor of Chemistry

In our studies on the behavior of highly reactive carbonium ions in model systems, we were concerned with the relative stereochemistry of the epimeric cis-2-decalylamines and cis-2-decalols (1). The experimental procedures involved have been optimized and the interpretation of the experimental results has led to unambiguous assignments of stereochemistry of these amines and alcohols. These conclusions and their consequences, in terms of behavior of carbonium ions along with our method of stereochemical assignments, have been submitted for publication (2).

During our studies of the amonolysis of tosylates of the above general type (l), we have discovered that 3β -tosyloxy- 5α -cholestane reacts with ammonia to form, not only a primary, but also a secondary amine. We now have adduced some evidence that this secondary amine arises from a carbonium ion intermediate rather than by a direct displacement mechanism.

In our efforts to study the behavior of another type of carbonium ion, we have been involved with the preparation of 3-phenylallylamine. At present, we are studying some of the chemistry of a potential precursor, 3-phenylallylisocyanate. We intend to resolve the 3-phenylallylamine and use optically active amine for some experiments, i.e., deamination to produce a carbonium ion. This will allow us to use the optical activity of the products as one criterion of carbonium ion behavior.

- (1) J. Pinkus and T. Cohen, First Annual Report, 1 May 1964.
- (2) T. Cohen, M. Malaiyandi, and J. Pinkus, J. Org. Chem., in press.

THE REACTION OF ISOCYANIDE SYNTHESIS WITH DIBORANE by John Tanaka, NASA Postdoctoral Research Fellow in Chemistry

The major portion of time between February 1 to July 1 was spent in working out a synthesis for completely deuterated trimethylamine. The first two schemes worked out were found to be unsatisfactory because of hydrogen-deuterium exchanges taking place during the Hoffman elimination reaction (1). The third scheme has been shown to yield completely deuterated trimethylamine. Deuterated methyl iodide was condensed with deuterated ammonia in silver oxide and heavy water. The quaternary ammonium deuteroxide which resulted was pyrolyzed to yield deuterated trimethylamine and dimethyl ether. The reaction is currently being scaled up so that enough material can be prepared for the determination of the various physical properties of completely deuterated trimethylamine.

Since July 1, 1964, the major portion of time has been spent in studying the reaction of diborane with phenylisocyanide. At the present time it is thought that the reaction involves an initial adduct formation of a BH3 group on the carbon of the isocyanide. This adduct apparently undergoes an easy hydride shift to form the compound $\vec{N} = C < \frac{H}{BH0}$

That this rearranged product easily reacts with another BH₃ group has been demonstrated. The structure of the monoadduct is consistent with its infrared spectra. It has also been shown to exist in a dimeric form by a molecular weight determination.

A short paper (Thin-Walled Pyrex Capillaries for Single-Crystal X-ray Diffraction of Pyrophoric Compounds) resulted from work done between September 1963 and January 1964 (2).

- (1) J. Tanaka, First Annual Report, 1 May 1964.
- (2) J. Tanaka and E. L. Amma, Review of Scientific Instrument 35, 634 (1964).

INVESTIGATION OF THE SCATTERING OF SEISMIC WAVES FROM GEOLOGIC DISCONTINUITIES

рà

Walter Pilant, Associate Professor of Geophysics

The calibration of the direct digitization facilities of the model seismic laboratory has been completed. There are some problems associated with vertical and horizontal amplifier drift in the oscilloscope which manifests itself as a limitation upon the accuracy in amplitude and time delay. However, the accuracy obtainable at present is comparable with that obtained by manual methods of reading photographic records of the oscilloscope trace which have been used previously. The time saving in this method (compared to manual digitization) is approximately ten to one and operator inaccuracy is considerably reduced.

The first problem selected was the completion of the work on reflection and transmission coefficients of Rayleigh waves around an edge. Previous work at another institution had given experimental values for included angles of solid material ranging from 40° to 180° . The work is now being extended to angles from 180° to 270° . Theoretical first approximations have indicated symmetry about 180° , and the accuracy of these approximations is to be investigated experimentally.

This particular problem is the simplest conceptual model of the effects of the earth's topography upon seismic surface waves, and is related to the larger problem of the effects of continental margins and mountain ranges upon the propagation of surface waves on the earth. It is hoped that from these investigations some diagnostic techniques may be developed which will aid in the quantitative determination of some of the parameters of these tectonic irregularities of the earth's crust.

The direct digitization techniques are particularly applicable to the determination of loss mechanism in rock and other crystalline materials. At the completion of the determination of the reflection and transmission coefficients mentioned above, a number of measurements will be made in this area to establish whether a significant improvement can be made in the determination of loss and loss mechanisms in such materials.

EARTH SCIENCES OBSERVATORY AND EQUIPMENT by Ralph Wyckoff, Professor of Geophysics

Progress has been made in securing a site for use as an observatory for seismic, earth tides, magnetics and possibly other phenomena of importance in earth science studies. The proposed facility is an abandoned "Nike" site but necessary building modifications were delayed for months until property transfer negotiations could be completed. Presently we are awaiting connections to power lines and, additionally, heat and control facilities must be added since the military recently and unexpectedly removed the airconditioning installation without which the building is untenable. As soon as possible, instruments will be installed to test the suitability of the site for the proposed future operations. In particular the ambient noise level of seismic disturbance must be determined before any investment in a suitable underground vault can be made.

Seismic Tests

These preliminary seismic tests will be made with the instruments placed on the concrete floor of the small Nike Control building which ultimately will house the recording equipment. The floor slab appears to be solidly based and adequate for preliminary tests. The following seismograph instruments are presently available:

- 1 Benioff short period vertical, variable reluctance
 type.
- 2 Wenner horizontal pendulums, reconditioned. Suitable long and short period galvanometers together with photo recording drums are available to complete the installation.

Should the site prove satisfactory more modern equipment is contemplated.

Earth Tide Equipment

Gravimeter - A LaCoste-Romberg "Microgal" recording gravimeter has been on order for some six months and the manufacturer reports good progress. Because of the necessity for prolonged observation of performance at the factory it will probably be March or April 1965 before delivery can be expected. Selection of this instrument is based on the proven performance of several units that have produced excellent results at other observatories. The instrument will be equipped for digitized output to facilitate computer analysis of the data.

Ralph Wyckoff Page 2

We are not seriously concerned about the suitability of the station site for this gravity-measuring device.

Tidal Tilt Meters - We have on hand two new all-quartz horizontal pendulums of Royal Observatory of Belgium design and construction as used extensively worldwide by earth-tide observatories. A suspension fibre in one instrument, broken in transit, will require repair, otherwise the equipment is complete with optical recorders and calibrating devices.

The extreme sensitivity of tidal tilt meters will preclude satisfactory use in any preliminary tests and possibly even in an underground vault on this site but this type of equipment must be available. A satisfactory site usually involves an underground station in a massive rock formation.

Magnetics - While magnetic observations are not included in immediate plans we will have available suitable recording flux-gate magnetometers to test the site for cultural noise down to the fractional gamma range. The site should certainly be satisfactory for normal magnetic variation observations but some micro-pulsation studies might be desired.

Experimental Studies - Tidal tilt meters are customarily designed for optical recording only and because of the nature of the horizontal pendulum design they are not amenable to direct digital recording. However, in common with tidal gravity data, machine analysis is highly desirable. Accordingly some laboratory work has been done to determine the practicability of a compact photo-electrically activated servo system to convert a light-beam deflection into an electrical signal amenable to digital recording.

The experimental setup exhibited no stability problems and the nature of the system eliminates to a high degree errors due to normal variations in light intensity and amplifier gain. Final evaluation requires tests on a unit designed for a specific application, but the system appears to be applicable from the very long periods involved in tidal observations to periods of one second or less as encountered in teleseismic observations.

GENERAL RELATIVITY

bу

Alan H. Thompson, Assistant Professor of Mathematics

The group whose work is here reported consists of myself and two research students, Mr. R. Reynolds and Mr. R. Roman. Dr. G. Williams (University of Florida) also worked with the group for two months during the period covered by this report (See his report).

Mr. Reynolds and Mr. Roman have continued their projects outlined in the last report.

My work has been concerned with the generalisation of results already obtained for time-like Conformal Killing Vectors to time-like congruences of curves which are restricted only by the fact that they do not shear. The physical description of such curves is that of a relativistic fluid moving in such a way that a fluid element has the freedom to expand and rotate but not to distort its shape.

Abstract:

We consider the space-time of relativity--a normal hyperbolic Riemannian 4-Dimensional Space V4 of signature +2. The metric is supposed to be given by g_{ab} ; and there exists a time-like congruence of curves defined by the contra-variant vector field u^a , which is non-shearing,

i.e.,
$$g_{ab}u^{a}u^{b} = -1$$
 and $\perp u_{(a;b)} = 0$.

Here the symbol \perp denotes projection of all following indices by the operator $h_a{}^b = \delta a^b + u_a u^b$ and $T(ab) = 1/2 (T_{ab} + T_{ba})$. In terms of the Lie Derivative this restriction can be written

where $\theta = u^a$; a is the expansion of the congruence. The object of the research is to find the integrability conditions for the equation (1), analogous to those found by Pirani and Williams for Rigid Motion, i.e., for the equation

$$\chi_a^a h_{ab} = 0.$$

Note: [A rigid motion is a non-expanding shear-free motion]

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The method of approach involves a transformation to a certain space $\overline{V}\mu$ which is conformal to the $V\mu$ under consideration; e.g., if g_{ab} is the metric tensor of $\overline{V}\mu$ then

$$\overline{g}_{ab} = e^{2\psi} g_{ab} \quad \psi = \psi(\psi^a)$$
.

We associate the congruence $\bar{u}^a \in \bar{V}_\mu$ with the original congruence u^a : $\bar{u}_a = e^{\psi}u_a$, $\bar{u}^a = e^{-\psi}u^a$, and hence in \bar{V}_{μ} $\bar{u}^a\bar{u}_a = \bar{v}_{\mu}$, that is \bar{u}^a is the unit tangent to a time-like congruence of curves in \bar{V}_{μ} . We note that the quantities of shear and rotation (\bar{v}_{μ} \bar{v}_{μ}) are relative invariants under conformal transformations; i.e., if σ_{ab} and $\bar{\sigma}_{ab}$ represent the shear of \bar{u}^a and \bar{u}^a respectively then

$$\overline{\sigma}_{ab} = e^{\psi} \sigma_{ab}$$
.

Thus the "shear-free" quality of a congruence is preserved under conformal transformations. This does not hold for the expansion and we can always find a $\overline{V}4$ and \overline{u}^2 conformal to the given V_{l_1} and u^a such that its expansion vanishes. We are thus able to associate with a shear-free congruence, a rigid congruence under a conformal transformation. By taking the conformal transformation of the known integrability conditions for a rigid motion we hope to generate those for equation (1) and thus be in a position to discuss such questions as the conformal generalisation of the Herglotz-Noether Theorem.

A further topic under discussion is that of a space-time which satisfies the relation

$$R_{abcd;ef} = K_{ef} R_{abcd}$$
 (2)

where R_{abcd} is the Curvature Tensor of the Space and K_{ef} (\neq 0) is a two-index tensor field. This is a generalisation of Ruse's "Spaces of Recurrent Curvature," and such spaces satisfy (2). It would be interesting to see if there are any more such spaces which do not have Recurrent Curvature:

Preliminary results are that $K_{\rm ef}$ must be a symmetric tensor, and that if the space is an Einstein Space $[R_{\rm ab}$ = 1/4 $R_{\rm gab}$] then the scalar curvature R of the space must be zero and it is thus a special Einstein Space.

GENERAL RELATIVITY

by

Gareth Williams, Visiting Associate Professor of Mathematics (April 16, 1964, to June 15, 1964)

A series of lectures was given to the Pittsburgh relativity group on "Rigid and Related Motions in a Gravitational Field." The classical definition of rigidity that Euclidean distance between any two points be independent of time was shown to break down in the Special Theory of Relativity and hence in the General Theory also.

A definition of rigidity in Minkowskian space-time, based on the concept of distance between neighboring particles was proposed, first by Born (1) and has since been discussed by Herglotz (2) and Noether (3), Synge (4), Rosen (5), Salzman and Taub (6), Pirani and Williams (7). According to this definition, a body is called rigid if the distance between every neighboring pair of particles, measured orthogonal to the world-line of either of them, remains constant along the world-line. The equations of rigid motion were derived and by using a special rigid coordinate system the integrability conditions were obtained.

Consequences of the integrability conditions were discussed. It was shown that the angular velocity of a heavy rigid body must be constant. The same result was also shown to apply to a rigid test body.

The Herglotz-Noether Theorem that in flat spacetime every rotating rigid motion is isometric was derived and extended to spaces of constant curvature. That the Herglotz-Noether Theorem does not hold for arbitrary space-times was shown by constructing a transformation of space and of motion that violated the isometric condition without annihilating the angular velocity.

The series was concluded with a discussion of non-rotating rigid bodies. It was shown that such a motion is isometric if, and only if, the metric is static.

* * *

Possibilities of extending the Herglotz-Noether Theorem to Homothetic Motions (8) and Conformal Motions were discussed with Professor Thompson and his colleagues. Preliminary investigations have shown all Conformal Motions, and hence all Homothetic Motions to be shear-free. In a space of constant curvative (other than Flat Space) all Homothetic Motions were found to be isometric. As an

analogue to rigid motion, a motion restricted by the condition of having to satisfy the homothetic condition in the three-dimensional space orthogonal to the world-line was investigated. It was found that such a motion when expansion-free degenerated into a rigid motion.

* * *

The possibility of classifying four-dimensional spaces of signature +2 with corresponding geodesics was investigated. A quasi orthogonal ennuple as defined by Wong (9) was used. hab and gab being the metrics of the two spaces, the trace-free, symmetric, second-order tensor L_{ab} was defined by $L_{ab} = h_{ab} - 1/4 \text{ hg}_{ab}$, $h = \mathbf{g}^{ab}h_{ab}$. The eigenvectors for L_{ab} , for [31] and [211] were used to construct a quasi orthonormal tetrad. The case in which the elementary divisors of $|L_{ab}-\lambda g_{ab}|=0$ are simple has been considered by Eisenhart. For a Riemannian Space of signature +2, the remaining cases are those for which the Segné characteristics of L_{ab} are [31], [211], together with their subcases [(31)], etc. In the [31] case the null eigenvector is shown to be expansion-free, geodetic, shear-free and irrotational. The space-like eigenvector is found to be geodetic, irrotational but not expansion-free nor shear-free. A similar investigation of the eigenvectors for the [211] case is underway. From the tetrad the metrics will be constructed and their properties discussed.

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ATOMIC COLLISION PROCESSES

bу

W. L. Fite, Professor of Physics,

- R. T. Brackmann, Research Assistant Professor of Physics and Electrical Engineering, and
 - W. R. Henderson, NASA Postdoctoral Fellow in Physics

Heavy Ion Collisions

During the past six months the principal activity has been the measurement of charge transfer and electron stripping cross-sections in collisions between Al⁺ ions and atmospheric gases, at energies in the 100 keV range.

Interest in this problem originates from questions pertaining to the duration of entrapment of debris in the magnetic field of the earth. The debris might come either from nuclear weapons or from propulsive devices which emit energetic heavy ions. While a great deal of work on charge transfer involving very light ions and ions of the inert gases, many questions arise in connection with heavy metallic ions, for here the first and second ionization potentials are small and one might expect ion stripping to a much more prominent competitor with charge transfer neutralization than in the inert gas ion case.

The program of measurements involves the use of the 500 kev Van de Graaff machine of Prof. Donahue and the new two-stage vacuum system and accompanying modulated beam electronics which was constructed by Fite and Brackmann after arrival at Pitt. The experiments are conventional fast-particle detection experiments.

In May the case of Al⁺ ions against Ar, N₂ and O₂ came under direct experimental study and measurements were made of the charge neutralization cross-sections of singly charged ions, δ 10, the charge stripping cross-sections, N₁₂ and total neutral loss cross-sections σ ₀ (which occurs principally through stripping of an electron from the neutral). Some information was also obtained about the angular deflections suffered in charge changing collisions. The energy range has been 50 key to 500 key.

Generally the experiments have borne out the suspicions that stripping of the ion is much more prominent than in the cases of non-metallic ions, and that the equilibrium fractions of fast Al passing through normal gases would contain substantially more singly and doubly charged components than neutral component.

The cross-sections have been collected with lower energy cross-sections for the same reactions and have been

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summarized in General Atomic Report GA 5518. (The measurement of these cross-sections is done at Pitt under contract with General Dynamics/General Atomic, which has a prime contract from Air Force Weapons Laboratory for the overall program of measurement.)

In more recent times, preparations have been made for repeating the same types of measurements, but with the primary ion being Fe+ A satisfactory iron ion source has been constructed (primarily by Mr. William Ott, a graduate student) and tested, and is currently being used for the cross-section measurements. It is planned that following the measurements using iron ions, the program will move next to uranium ions.

Hydrogen Atom Collisions

For the pursuit of a series of very difficult measurements on certain collision cross-sections involving hydrogen atoms as one of the colliding particles, a proposal had been submitted to the National Science Foundation last spring. We recently received word that a grant has been given for this work. Unfortunately, because of tightness of funds the amount of the grant will not enable us to construct the highly sophisticated modulated atomic beam: machine that will be required for the most difficult (and interesting) of the measurements we desire to attempt. However, this initial grant will enable us to construct some of the specialized equipment, and will permit a limited program of hydrogen atom collision cross-section measurements to be gotten under way. Because of increasing interest in metastable hydrogen atom in the 2S state, both from the points of view of basic theory and of astrophysics, we currently incline initially to emphasize work involving the metastable H atom.

Currently, detailed design of those portions of equipment which can be constructed and procured under the initial NSF grant is the major activity in this program.

Collisions with Excited Molecules

Interest in studying collisions with excited molecules originated with the observation by Fite and Brackmann about 1 1/2 years ago that if O_2 is heated to around 2000° K, its cross-section for forming O^- through the process $e + O_2 \rightarrow O + O^-$ appeared to increase and the dependence on energy seems to change dramatically. The presumption is that upon heating, the O_2 becomes partially excited and what was being observed was a striking difference between the collision properties of ground state and excited molecules.

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At the time of the initial experiment, there was no way to discern what type of excitation (i.e., electronic or vibrational-rotational) was responsible for the effect. However, if the experiment were to be repeated using an electron gun with a very narrow energy spread, the prognosis is good that the actual states involved in the effect could be identified.

To this end Dr. Watson R. Henderson, who arrived as a postdoctoral fellow from the University of Texas in September, is constructing the required monoenergetic electron gun. It is a spherical analyzer type.

This experiment will involve using the two-stage vacuum chamber which is currently in use in the heavy ion collision program. A beam of heated O_2 (and other gases) will be formed and modulated, and the electron beam will cross the molecular beam. Ions formed in the collisions will be analyzed using a rf quadrupole mass filter (which is nearing completion). The experiment is a straightforward application of modulated beam mass spectrometry and should yield early (as well as exceedingly interesting) results.

We have received reliable although informal word that this work will be supported by the Defense Atomic Support Agency of the DOD through the Army Research Office, Durham.

ATOMIC PHYSICS - THEORETICAL by Edward Gerjuoy, Professor of Physics

During the past six months, I have prepared and submitted for publication to the Annals of Physics a long paper, "Multi-Wave Propagation and Causality," which may have a bearing on the propagation of whistlers in the atmosphere; whistlers are electromagnetic waves of very low frequency which propagate in the ionospheric plasma and are believed to be generated by lightning discharges. For the foreseeable future, I plan to continue working on the theoretical prediction of various reaction rates relevant to understanding of upper atmospheric phenomena. In particular, I expect to work on developing new procedures (variational and/or modified Fredholm integral techniques) for computing such reaction rates. During the next few months, I will be working on a review paper "Electron-Atom and Electron-Molecule Scattering Theory Circa 1964," which I have been invited to present at the December, 1965, New York meeting of the American Physical Society.

MEASUREMENTS OF CHARGE EXCHANGE AND

IONIZATION CROSS SECTIONS

рy

Kotu Lulla, NASA Postdoctoral Fellow in Physics

The following report covers work done in the laboratory of Professor T. M. Donahue in the Department of Physics, Space Research Coordination Center, University of Pittsburgh, since July, 1964.

Electron Loss

The products of collision left behind when atomic hydrogen beam of 5-50 kev traverses CO gas have been analyzed with a quadruple mass spectrometer of mass resolution, $\frac{\Delta M}{M}$, of 1/60. O and CO are the only ions found in abundance. This suggests that the main electron loss process is

$$H + CO \longrightarrow H^+ + C^* + O^-$$

where neutral C atoms may be left in the ground or excited state. The other possible process for electron loss is

$$H + CO \rightarrow H^{+} + C^{*} + O^{*} + e$$

The simultaneous measurement of σ_{Ol} cross section and mass analysis will enable us to determine the processes responsible for structure in σ_{Ol} curve as a function of energy (1).

In the near future we plan to conduct similar studies for gases such as O_2 , H_2 , etc.

Charge Exchange

The construction of the apparatus for the study of charge exchange in H(30 kev) + H⁺ (50 - 400 kev) collisions is progressing. The high current-duoplasmatron ion source and 90° bending magnet provide mono energetic proton beam of 10-30 kev. The search for a good donor gas for converting protons to H atoms with minimum pumping requirements is underway. Preliminary results indicate 50% conversion for 20 kev protons with alkali vapor (K). The next step will be to cross the neutral atomic hydrogen beam with a beam of a 400 kev proton Van de Graaff accelerator.

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THERMOLUMINESENCE IN QUARTZ

bу·

M. Schlesinger, NASA Postdoctoral Fellow in Physics

In the attempt to gain a better understanding of the thermoluminescent phenomena in quartz, the technic of re-excitation by u.v. light was applied, along with parallel optical-EPR measurements.

Some of the results are briefly summarized in the following abstracts of two papers to be presented at the American Physical Society meeting taking place in Chicago during November, 1964.

The measurements hitherto were carried out for temperatures above liquid nitrogen temperature. It is planned, however, to extend them below that, down to liquid helium temperature. The thermal activation energies of traps responsible for some of the glow peaks were determined by the so-called "Initial Rise" method.

1. Re-Excitation of Glow Peaks in the Glow-Curves of Quartz

Illumination with monochromatic light into various color-center absorption bands of quartz at liquid nitrogen temperature (LNT) after previous x-irradiation at room temperature (RT) re-excites some glow peaks of the "usual" glow-curve in the region between LNT and RT. Re-excitation can also be performed for peaks above the temperature at This can be done which the crystal was x-irradiated. after previously raising the temperature above that of the peak to be re-excited. A plot of re-exciting efficiency vs. wavelength follows, for Ge-doped crystals, their absorption in the vicinity of the = 280 mm absorption band. Illumination in the \approx 450 m μ "aluminum" band causes no The effect has been investigated in detail re-excitation. for crystals doped with various impurities and under various conditions. The present work shows that the effect is an efficient means for resolving absorption bands introducted by x-irradiation which were hitherto unresolved in usual absorption measurements. It also adds to the understanding of the thermoluminescent process in quartz.

2. Effects of Heating on Color Centers in Germanium-Doped Quartz

(Frank J. Feigl, M. Schlesinger, and John H. Anderson.)

Thermoluminescence, light absorption, and electron spin resonance (ESR) have been measured in x-irradiated, germanium-doped quartz crystals having three different compositions. The phenomena were found to be correlated

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in the following sense: Maxima of (1) thermoluminescence intensity, (2) bleach rate of the $\approx 280~\text{m}\mu$ absorption band, and (3) decay rate of the A and C ESR lines occur at the same temperature. This temperature is 600°K for two crystals and 460°K for the third. Optical data were obtained by making a series of rapid scans of the spectrum while heating the sample at the same rate used for glow curves. The relation dA/dT α I, where A is absorption at 280 m μ , T temperature, and I thermoluminescence intensity, is approximately satisfied. Optical and ESR results strengthen the hypothesis (1) that both are due to electrons trapped at substitutional Ge atoms. Their correlation with thermoluminescence supports the suggestion (2) that thermoluminescence results from release of electrons from Ge centers which then recombine with holes at Al sites.

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LABORATORY STUDIES ON COLLISION PROCESSES OF

AERONOMIC INTEREST

by

Edward C. Zipf, Jr., Assistant Professor of Physics

The $A^3\Sigma_u^+$ state is the lowest excited, electronic state of nitrogen. Radiative transitions from the levels of this state to the ground state are forbidden by a spin selection rule and, as a consequence, the state is metastable with a radiative lifetime of several seconds (1), (3), (4), (6). In spite of this comparatively long radiative lifetime, nitrogen molecules in the metastable $A^3\Sigma_u^+$ state are sufficiently abundant in most auroras and some laboratory discharges so that they can be detected through observation of the forbidden Vegard-Kaplan bands,

$$N_2(A^3\Sigma_u^+) \longrightarrow N_2(X^1\Sigma_g^+) + h\gamma$$
 (1)

The brightest bands of the Vegard-Kaplan system are emitted in the ultraviolet region of the spectrum and they are the dominant feature in the auroral spectrum from 2000 Å to 3000 Å (2).

The processes by which nitrogen molecules in the $A^3\Sigma_u^+$ state are destroyed in an aurora have been studied in considerable detail in the laboratory (5), (6), (7), (8). During the period covered by this report we have been particularly concerned with the possibility of a quadratic loss mechanism (metastable-metastable collisions) involving $N_2(A^3\Sigma_u^+)$ molecules. From an analysis of a limited amount of laboratory data we have concluded that this process is the dominant loss mechanism for nitrogen molecules in the $A^3\Sigma_u^+$ state when the density of these metastable molecules is comparatively high ($\sim 5 \times 10^{11} \text{ cm}^{-3}$). The following reaction scheme appears likely,

where the N₂* denotes a vibrationally excited ground-state molecule and N₂($^5\Sigma_g^+$) denotes a $^5\Sigma_g^+$ molecule that has been formed in the dissociation continuum of the state. This molecule is unstable and in a comparatively short time dissociates into two 4S atoms which possess about 1.2 ev between them in the form of kinetic energy.

The ratio of the rate coefficient for this process, k, to the radiative transition probability for the (0,6)

Edward C. Zipf, Jr. Page 2

Vegard-Kaplan band, A(0,6), has been determined and at 300° K k/ $A(0,6) = 3 \times 10^{-9}$ cm³. This is the first successful attempt to observe metastable-metastable collisions involving diatomic molecules, and these results have been reported at the 17th Gaseous Electronics Conference (October 14-16, 1964) (8).

Additional laboratory studies on collision processes of aeronomic interest are planned and the development of suitable laboratory apparatus for this purpose is our immediate goal. In addition, we plan to extend our analysis of existing data on the ${\rm A}^3\Sigma_{\rm U}^+$ state to higher vibrational levels and to assess the role played by thermal electrons in the deactivation of this state. We also plan to complete the calculation of the excitation of the first and second positive systems of ${\rm O}_2^+$ in the dayglow through simultaneous excitation—ionization of ${\rm O}_2$ by solar EUV radiation and compare the calculated results with previously obtained rocket data.

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COMMUNICATION BY ELECTRICAL STIMULATION OF THE SKIN by
Robert H. Gibson, Associate Professor of Psychology

General

This report covers the summer period of a research program on communication by means of electrical stimulation of the skin senses. Equipment development and modification, experiments on tactile sensory properties and on tissue electrical characteristics, and a computer program are described. The research reported is part of a three-year program supported partly by NSF (B-15440), by NIH (NB05099-01), by an institutional grant from NSF to Carnegie Institute of Technology, and in part by an institutional grant to the University of Pittsburgh from NASA.

During the report period the project was moved with the principal investigator from Carnegie Institute of Technology to the Psychology Department of the University of Pittsburgh. In June, an M.S. thesis, entitled Spatial Factors in Electrical Stimulation of Touch, was completed under project support and submitted to Carnegie Tech by James R. Milligan. A 30-minute talk, entitled Effects of Temperature on Touch, Pain and on Tissue Electrical Properties was delivered in October by R. Gibson to the annual meeting of the Psychonomic Society at Niagara Falls, Ontario.

Introduction

Various attempts to devise cutaneous communication systems as supplements to vision and audition have been made over the past century. None has provided the speed or complexity comparable to information transmission through visual or auditory channels. Rather than reflecting limiting properties of the touch sense, the limited nature of cutaneous communication reflects the failure best to use properties of touch perception.

To find whether cutaneous channels are effective for more than simple, unidimensional warning information, or slow speech transliteration, it is essential to determine perceptual properties of stimuli varied systematically along temporal and spatial dimensions. One impediment for acquiring such knowledge has been poor stimulus control. Unlike mechanical stimuli such as from vibrators, which are impeded in their movement by their own mass and by tissue factors, electrical stimuli, as light and sound signals, are capable of a wide range of temporal variation. Until recently, electrical skin stimulation readily excited pain and thereby saw limited use. Now, procedures (1,2) have

been worked out in detail for painless electrical stimulation of the touch system. Brief (0.5 msec.) pulses of Anodal direct current, when combined in short trains, at low pulse and train repetition rates, and through sufficiently large electrodes, delivered by constant current stimulator so that peak current does not vary with tissue impedance, reliably can arouse painless touch.

The remainder outlines progress on a program of psychophysical experiments with electric stimuli aimed at contributing to basic sensory knowledge in three overlapping areas: (i) stimulus control, (ii) perceptual properties of touch, and (iii) cutaneous communication.

Projects

1. Multiple Dimension Stimulus Control System

The research to date has been designed to acquire data on basic sensory and perceptual phenomena mainly in their static states, one stimulus (or pair) at a time. Yet, the perceptual nature of absolute location phenomena, apparent motion, etc., all may change markedly in a dynamic situation where spatial and temporal patterns are changed rapidly and repeatedly over time. Thus, we devised a system to control multiple dimension stimuli. This system will be used in latter stages of the equal-loudness and apparent-motion studies, and is required for a multiple-target tracking project planned for next year.

The general problem for the system is to deliver rapidly a number of pre-programmed cutaneous electrical stimuli, different as to several stimulus parameters as well as the number of electrode locations on the body simultaneously stimulated. A specially constructed block tape reader that optically reads 96 bits of information each step, at a maximum rate of 10 steps per second, is the heart of the system. There are six independent channels, each multiplexed to 8 electrodes, a total of 48 locations on the body. All logic circuitry has been breadboarded and checked out, and construction is 25 per cent complete. A draft for a manual of description and operation is substantially complete. A tape library of varied stimuli is being prepared.

2. Electrical Thermode

A thermoelectric element, using the PELTIER effect to generate rapid temperature change proportional to the quantity of electricity passed through a junction, was attached to a machined brass electrode and built into essentially a beam balance so as to control electrode pressure.

Attaching the proper heat sink to the upper plate of the element enables a delta-temperature between upper and lower plates of 55°C. Based on rough calculations, a 7-watt heat load is supplied by the tissues of the dorsal forearm to a one square inch area; thus the temperature can be quickly varied (15 sec./°C.) from cold, through neutral, to warm, without being moved on the skin, a distinct advantage for threshold reliability.

3. Skin Temperature Effects on Touch and Pain Sensitivity

This is part of a larger effort to determine factors in electricity that underlie cutaneous stimulation so as to elucidate sensory mechanisms of operation.

Touch and pain thresholds were obtained from several observers under a variety of controls and conditions, most of which were aimed at increasing the precision of measurement.

Effects of temperature variation of 15°C to 45°C, the tolerable range, on electrical touch sensitivity were slight or nonexistent. Thus, the site of excitation of the touch system by electricity is probably directly at the nerve itself, beyond the receptor potential, since the rate of increase of this potential with a constant amplitude stimulus varies directly with temperature.

Contrary to expectations, the results with stinging pain on hairy tissue suggest an approximately U-shaped function relating pain threshold as peak current to temperature, with maximum sensitivity to pain near room temperature. However, pain thresholds were highly variable, despite extraordinary precautions to obtain regularity by reducing effects of extraneous variables, implying either a basic instability in the pain mechanism, or further variables for study. Several observations suggest the latter, that thresholds vary from tissue properties independent of sensory mechanisms.

A stinging pain from electrical stimulation might simply reflect tissue breakdown from peak voltages developed across high resistance portions of the tissues that exceed the dielectric breakdown voltages, thus causing pain from sudden high current density at a spot. This notion will be followed up both (1) by using means for reducing tissue resistance thus the voltage required to stimulate with a given current, and (2) by monitoring 4 parallel segments of an electrode separately, each on its own oscilloscope trace, to see whether the voltage developed between any segment and its ground increases suddenly relative to the other segments at pain threshold.

4. Electrical Properties of Tissue

The purpose was to determine electrical properties of tissue stimulated with pulses of direct current. The more general aim is to relate tissue properties to sensory events.

The time-properties of voltage-current relationships within tissue were determined by recording the voltage response to current pulses of 1.0 to 50 msec. duration delivered by constant current stimulator with high output impedance (effectively 200 megohms).

The voltage led through hairy and hairless tissue on five observers was examined as a function of (i) peak current amplitude, (ii) electrode size, and (iii) skin temperature. The voltage developed across the two electrodes (large indifferent electrode on the sole of the foot, small active electrode on either the dorsal forearm or the palm at the base of the thumb) was displayed on one trace of a Tektronix 56l oscilloscope, the current pulse displayed on another trace, and both photographed.

It was found that the current rises nearly instantly to maximum, but the voltage lags, as in a capacitative circuit with the rate of rise, as well as the peak voltage at any given current, a function of the variables investigated. Therefore, (i) the peak voltage, and (ii) the time constant of voltage growth were measured from enlargements of the oscilloscope photographs as a function of the three variables.

Results were: (1) as current increases from 0.05 to 5.0 peak milliamperes, tissue peak resistance decreases, initially precipitously, then more slowly with further current increase. The decrease is from higher than 250 kohms, to less than 10 kohms, from 0.05 ma to 5.0 ma. The relation between peak resistance and peak current is hyperbolic with an exponent nearly unity; double the current, the peak resistance is nearly halved. (2) The time constant falls in the same manner as the peak resistance (although with a slightly greater exponent) with a peak current increase. The variation in time constant can be accounted for largely in terms of the fall in peak resistance. tissue resistance primarily, not membrane capacitance, is affected by the passage of current. It is reasonable to assume that most of the tissue change is in the surface layers, for they represent a large percentage of the total interelectrode resistance. Future plans include (1) following up this hypothesis by manipulating surface tissue resistance, and (2) determining the relation between

rapid tissue resistance changes and sensory thresholds. In a more practical vein, it is clear that it is not safe to stimulate human tissue with electricity, either for touch perceptual research or therapeutic purposes, without use either of constant current stimulators or rapidly acting current limiters. Also, to our surprise, owing to the large decrease in tissue resistance with the passage of, say only 100 peak microamperes for 1.0 millisecond, peak voltage requirements for satisfactory constant current operation in the 0.1 to 5.0 milliampere region is clearly possible with peak voltages of less than 60 volts. This makes transistorized constant current units feasible for portable communication devices.

5. Computer Simulation of Tissue Voltage Response

The nature of the voltage rise, with a rectangular step of current, and its dependence on current, electrode size, temperature, and certain polarity effects not discussed here, imply a dynamic circuit with resistances and capacitances varying nonlinearly over time. fore, such circuits are difficult to solve with simple circuit theory. As a beginning, two computer programs were written to produce as output plots of voltage versus time. One program produced an approximation to our pictures by plotting the appropriate exponential growth. The other, and more promising, used the SCADS subroutines at Carnegie Tech's computation center; SCADS = Simulation of Combined Analogue Digital Systems. The final version of this program sets up an analog circuit that approximates a parallel R-C network with a large, variable series resistor to assure constant current. The output of this program closely approximates some oscilloscope pictures. The next step is to fill in appropriate circuit element values.

6. Equal "Loudness" Functions

Threshold peak current (with 0.5 msec. pulses) and the "loudness" of suprathreshold electrical stimuli vary with (i) train duration, (ii) repetition rate, (iii) electrode size, and (iv) the number of electrodes on a given body region (i.e., interelectrode distance). Thus, these variables cannot now be simply manipulated without simultaneously monitoring peak current. Equal "loudness" functions are being obtained for these variables on several body regions. The observer matches the apparent intensity of one stimulus to that of another. Such functions will provide normative data that make it feasible in further experiments to manipulate these variables in combination over wide ranges using the stimulus control system with only minor unplanned variations in apparent intensity.

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- (1) R. H. Gibson, Proceedings of the International Congress on Technology and Blindness 2, 183 (1962).
- (2) R. H. Gibson, Nature 199, 307 (1963).

APPENDIX A

NASA Postdoctoral Fellows

(name in parentheses is that of the cognizant faculty member)

Name	Ph.D. From	Year	Program
Helmut Ankel (Prof. E. Englesberg)	Univ. Marburg, Germany	1960	Polysaccharide synthesis of Cryptococcus laurentii
R. K. Duggins (Prof. C. C. Yates)	Univ. Nottingham, England	1962	Theoretical study of flow separation
Elli O. Hand (Prof. T. Cohen)	Harvard Univ.	1962	Study of reactions in heterocyclic compounds in which radicals serve as intermedicates
Watson R. Henderson (Prof. W. Fite)	Univ. Texas	1963	Electron collisions with excited atoms and molecules
Edgar Inselberg (Prof. J. Rosenberg)	Univ. Illinois	1962	Photosynthesis studies; re-examination of the statistical analysis of radio-assay
Truman H. Jordan (Prof. G. A. Jeffrey)	Harvard Univ.	1954	The investigation of the crystal structure of H2CO3.Ef20; the construction of an automated single crystal diffractometer
Kotu Lulla (Prof. T. Donahue)	New York Univ.	1964	Laboratory study of uper atmosphere atomic interactions, particularly charge exchange processes

APPENDIX A - continued

Мате	Ph.D. From	Year	Program
Thomas Mak (Prof. G. A. Jeffrey)	Univ. British Columbia	1963	Mode of formation of crystalline hydrates from gases; applications to planetary atmosphere studies
Jack L. Pinkus (Prof. T. Cohen)	Univ. Southern Calif.	1956	Study of solvolytic reactions in ammonia in which carbonium ions are intermediates
M. Schlesinger (Prof. J. Anderson)	Hebrew Univ., Jerusalem	1963	Optical absorption and thermoluminescence in materials containing color centers
John Tanaka (Prof. E. Amma)	Iowa State Univ.	1956	Chemical and structural studies of inorganicarromatic complexes; electron-deficient bonding in aluminum alkyls
S. Venketeswaran (Prof. C. Partanen)	Univ. Pittsburgh	1961	Study of radiation effects on albino mutants of tobacco cells to understand the mechanism of photosynthesis

APPENDIX B

NASA Predoctoral Trainees

Name	B.S./B.A. From	Year	Department	QPA Undergrad.	Graduate
Anthony Sobota	Indiana State College	1960	Botany	3.10	3.90
Edward M. Phillips	Lafayette College	1958	Chem. Eng.	3.15	new
J. M. Pommersheim	Univ. Pittsburgh	1959	Chem. Eng.	3.53	3.78
John J. Farrell	Baldwin-Wallace Coll.	1960	Chemistry	3.30	3.71
Nancy Heatwole	Madison College	1959	Chemistry	3.80	3.70
Joseph Natowitz	Univ. Florida	1958	Chemistry	3.12	3.58
W. W. Johnson	Univ. Utah	1956	EPS*	3.25	3.81
Nunzio A. Tartaglia	Manhattan College	1958	EPS*	3.91	new
Leo C. Geary	Univ. Pittsburgh	1964	Elec. Eng.	3.42	пем
David C. Opferman	Penn State Univ.	1961	Elec. Eng.	3.40	3.40
D. C. Jessep	Univ. Pittsburgh	1960	Elec. Eng.	3.70	0077
J. E. Peterson	Penn State Univ.	1957	Mech. Eng.	3.34	3.55
William R. Tilton	Univ. Pittsburgh	1963	Mech. Eng.	3.19	2.50
Robert L. Powell	Univ. Cincinnati	1957	Pharm.	3.23	3.65
Paul Demmie	Univ. Pittsburgh	1964	Physics	3.51	new
David Emin	Florida State Univ.	1962	Physics	2.76	3.46

*Earth and Planetary Sciences

APPENDIX B - continued

				QPA		
Name	B.S./B.A. From	Year	Department	Undergrad.	Graduate	
Charles Richter	St. Joseph's College Philadelphia	1964	Physics	3.40	пем	
Raymond Turner	Carnegie Inst. of Tech.	1960	Physics	3.07	3.28	
David L. Uhrich	Canisius College	1960	Physics	3.63	3.57	
Felix Ullrich	Rutgers Univ.	1961	Physics	3.08	3.33	
John A. Zelik	Univ. Pittsburgh	1963	Physics	3.55	3.43	
John M. Lyons	Loyola Univ., Chicago	1962	Psychology	3.41	3.60	
James W. McKearney	C. W. Post College of Long Island Univ.	1962	Psychology	3.79	4.00	

APPENDIX C

New Paculty Members for 1964-1965

(Division of the Natural Sciences, School of Engineering and KAS Center only)

Name	Department	Rank	Ph.D. From
Mark A. Bambenek	Chemistry	Assistant Professor	State U. Iowa, 1961
Jack Belzer	Indust. Engineering	Associate Research Professor	B.S. in E.E., Cooper Union, 1932
James J. Billings	Physics	Assistant Professor (Ecuador AID Project)	U. Texas, Austin, 1958
Hans C. Bjerring	Biology	Visiting Assistant Professor	Stockholm, 1964
Jacques-Emile Blamont	Physics	Visiting Professor	Ecole Normale Supérieure, Paris, 1956
Robert Bowen	RPS*	Research Assistant Professor of Geochemistry	U. London, 1953
Chao-Lin Chiu	Civil Engineering	Assistant Professor	Cornell, 1964
Wilfried Daehnick	Physics	Assistant Professor	Washington U., St. Louis, 1958
Donald A. Dukelow	Metall. Engineering	Assistant Professor	Carnegie Inst. Tech., 1957
Michael D. Puller	BPS*	Assistant Professor of Geophysics	Cambridge, 1961
Chien Ho	Biophysics	Assistant Professor	Yale, 1961

Name	Department	Rank	Ph.D. From
Thomas F. Jordan	Physics	Assistant Professor	Rochester, 1962
Frederick Kaufman	Chemistry	Professor	Johns Hopkins, 1948
Paul M. Kjeldergaard	Learning Res. Dev. Center;	Res. Assoc.; Assoc. Professor	Minnesota, 1960
Paul M. LeVasseur	Comp. Data Proc. Center; Mathematics	Assistant Professor of Mathematics and Computer Sci.	Paris, 1963
Edward G. Lidiak	#PS*	Assistant Professor of Geology	Rice, 1963
R. H. Pratt	Physics	Associate Professor	Chicago, 1959
Glenn B. Roudabush	Psychology	Assistant Professor	U. Washington, Seattle, 1963
Edward I. Salkovitz	Metall. Engineering	Prof. of Metallurgy and Physics	Carnegie Inst. Tech., 1950
Bert Schroer	Physics	Visiting Assistant Professor	Hamburg, Germany, 1962
Leslie L. Seigle	Metall. Engineering	Visiting Professor	MIT, 1951
G. P. Szegő	Elec. Engineering	Visiting Associate Professor	Pavia, Italy, 1956
Joseph J. Taber	Chemistry	Adm. Officer and Asst. Prof.	Pittsburgh, 1955
Harvey Wolfe	Indust. Engineering	Assistant Professor	Johns Hopkins, 1964
Kenzo Yagi	*S4E	NSF Senior Foreign Science Fellow	Tohoku U., Japan, 1949

^{*}Earth and Planetary Sciences

APPENDIX D

New NASA-SRCC Faculty Appointees

1. FREDERICK KAUFMAN, Professor of Chemistry.

Professor Kaufman received his doctorate from the Johns Hopkins University in 1948. He was Chief Physical Chemist with the Ballistic Research Laboratories of the Aberdeen Proving Grounds. His field of research is the study of gas reaction mechanisms at high temperatures and combustion problems.

2. LESLIE L. SEIGLE, Visiting Professor of Metallurgical Engineering.

Professor Seigle received the D.Sc. degree from MIT in 1961. He will be at the University of Pittsburgh from October 15, 1964, to April 15, 1965, on leave from his position as Manager of Research in Metallurgy at the General Telephone and Electronics Laboratory. His fields of research include thermodynamic properties of solids, diffusion theory in alloys, electrical and optical properties of thermoconductors.

3. GEORGE P. SZEGÖ, Visiting Associate Professor of Electrical Engineering.

Professor Szego received his doctorate in physics from the University of Pavia in 1956. He is currently associated with the Institute of Theoretical Physics of the University of Milan, but has been in this country since 1960 as Visiting Assistant Professor of Electrical Engineering at Purdue University (through 1962). During this period, he was also associated with the Control and Information Systems Laboratory. From 1962-1963, he was a Member of the Center for Control Theory of the Research Institute of Advanced Studies in Baltimore. More recently he has been associated with RIAS, a research subsidiary of the Glenn L. Martin Company, and with the Technological Institute of Northwestern University. Basically an applied mathematician, his research involves theory of dynamic systems and control theory and non-linear differential equations. He has been at Pittsburgh since September 1, 1964, and will be here until approximately mid-November.

4. EDWARD I. SALKOVITZ, Professor of Metallurgical Engineering and Physics.

Professor Salkovitz received his B.Sc., M.Sc., and D.Sc. (1950)--all in physics--from Carnegie Institute of Technology.

He is currently Head of the Metallurgy Branch at ONR and acts as Principal Consultant to the Chief of Naval Research, the Chief Scientist and their staffs. He will come to the University of Pittsburgh in February, 1965, and is considering work in areas of (1) liquid state of metals and alloys, i.e., electronic properties; (2) polymers--mechanical, thermal, electrical, and magnetic properties; application of tools and concepts of metallurgy and solid state physics to polymer research.